

CHEMICAL EXAMINATION OF DISTILLATE FUEL DEPOSITS FORMED DURING STORAGE

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INTRODUCTION

Storage stability of distillate fuels has been of modest concern for fuels made by refining processes based on straight run distillation. However, increasing quantities of heavy crudes are being run in refineries using catalytic cracking processes to increase the yield of middle distillate fuels. The cracked products, which contain chemically unstable species, are blended into straight run streams. The unstable components, although diluted by the blending, still exert a strong influence on deposit formation, particularly for long storage periods. The fuel instability is manifested by the formation of insoluble products which play havoc with filters and nozzles of engines.

Oxidation is involved in the undesirable reactions as are fuel components containing hetero-atoms such as sulfur, nitrogen, and oxygen. More than free-radical autooxidation is involved, however, since typical free-radical antioxidants are ineffective in controlling this instability and can be deleterious (1). Further, degradation is increased by the presence of organic acids with the stronger acids exerting significant effects (2).

In this paper, we utilize several experimental techniques to characterize the insolubles as an aid in understanding the chemical processes which control the undesirable instability. The deposits examined include ones formed in stressed, undoped straight run/light cycle oil (SR/LCO) blends and in similar blends to which acids were added.

EXPERIMENTAL TECHNIQUES AND PROCEDURES

LCO and SR from a US Gulf Coast refinery were blended in a 20/80 ratio. The samples were stressed under accelerated conditions of 80 degC for 7 or 14 days, equivalent to 1 to 2 yrs at ambient conditions. Suspended products of instability were removed by filtration and products adhering to the stressing flask were removed with gum solvent. After evaporation of the solvent, the filterable and adherent insolubles were dried in a vacuum oven at 75 degC. The acids used as dopants were dodecylbenzene sulfonic acid (DBSA), chloroacetic acid (CA), and p-t-butyl thiophenol (PBTP).

Elemental analyses of the insolubles were done by Galbraith Laboratories, Knoxville, TN. Stressed and unstressed fuel blends and deposits were titrated in a non-aqueous solvent with approximately 0.04 N alcoholic KOH. X-Ray Photoelectron

Spectroscopy (XPS) analysis was conducted at the Naval Research Laboratory, Washington, DC and Field Ionization Mass Spectrometry (FIMS) was performed at SRI International, Menlo Park, CA.

EXPERIMENTAL RESULTS

Elemental Analysis. Table I lists the results of elemental analysis of various deposits from the stress tests. The carbon, hydrogen, and oxygen contents were similar for the insolubles from all samples. Nitrogen was lower for the sample derived from the fuel doped with p-t-butyl thiophenol. Sulfur was significantly higher for the blends doped with sulfur compounds, both the DBSA and the PBTP. All of these concentrations fall within the range observed for insoluble material derived from other storage stability experiments. The low H/C ratio (0.9 - 1.0) along with the high nitrogen, sulfur, and oxygen values support the view that hetero-aromatic compounds are major participants in insolubles formation. Chlorine was found in the insoluble sample derived from the fuel blend containing 0.01 M chloroacetic acid. Insufficient sample was available to do the other elements for this sample.

Titration Curves. Non-aqueous titrations of the stressed and unstressed liquid fuels gives useful information on the disposition of the added acids. Typical curves are shown for the sulfonic acid in Figure 1 and for thiophenol in Figure 2. The fuel blends for these titrations were not the same as the stress test samples but the same observations apply. The titrations in Figures 1 and 2 were done on different instruments which used opposite polarity conventions. The titration curve for unstressed DBSA exhibits a very high initial emf compared to the fuel blank. This is characteristic of strong acids such as sulfonic acids. The inflection point for neutralization of the strong acid is about +100 mv. The initial emf for the stressed DBSA is still high but the curve demonstrates that much of the DBSA is not available in the fuel after stress.

The titration curve for thiophenol shows that most of this weak acid has reacted during the stress period. Further, the initial emf has shifted from +120 mv to -220 mv. This is indicative of the presence of a very strong acid, sulfonic acid. Although the titer for strong acid is low, a definite quantity is present.

In addition to titration of the stressed and unstressed fuel blends, the solid sediments formed during the stress were subjected to non-aqueous titration. Strong acid was found in the sediments from the DBSA and PBTP doped samples.

XPS Analysis. This spectroscopic analysis was applied to the solids, both filterable and adherent, formed in the 80 degC stress. This technique affords good qualitative information but is not completely quantitative at low (<1%) levels of atomic %. This is due to electrical charging of the specimen in the high vacuum. Data for a typical analysis of insolubles is shown in Table II. The information is tabulated as atom % as opposed to weight % for Table I. This fact plus the fact that hydrogen is not determined

by XPS explains most of the differences between the results in Tables I and II.

Chlorine was detected only in the CA doped sample but just above the noise level. Sulfur is enhanced in the sulfur doped samples. XPS can distinguish between different valence states of atoms. This was particularly helpful in examining the sulfur composition. As Table III shows, reduced and oxidized forms of sulfur were found in these insoluble sediments. It is noteworthy, however, that the oxidized form predominates in the samples doped with the sulfonic acid and the thiophenol.

FIMS Analysis. This mass spectroscopic method affords a molecular weight pattern for a sample. The solids were pyrolyzed on a temperature-programmed probe in the inlet of the instrument. Further description and use of this technique will be detailed in another paper of this symposium. The highlights of FIMS application to the doped samples are as follows:

- (a) Major peak at 326 mass units for DBSA doped fuel;
- DBSA mol. wt. is 326
- (b) Major peaks at 166, 214, and 330 for PBTP doped fuel;
- PBTP mol. wt. is 166, PBTP dimer mol. wt. is 330, and p-t-butyl benzene sulfonic acid mol. wt. is 214
- (c) No peaks specific to CA were found in the insolubles from fuel doped with this acid

DISCUSSION

A test for material balance was made for the added acids. This was accomplished by non-aqueous titrations of the unstressed liquid fuel, the stressed liquid fuel, the filtration rinses, and the insolubles dissolved in titration solvent (1 part toluene to 1 part isopropyl alcohol). The petroleum ether rinses contained minute amounts of acid, only slightly more than the solvent blank. Table IV itemizes the balance for DBSA. A significant amount of strong acid was found in the insolubles, at least for the samples to which 1.0 mmol/L of DBSA was added. The acid concentration in the liquid fuel after stress and filtration was definitely lower than in the unstressed fuel. In fact, the amount of insolubles formed increases linearly with the decrease in DBSA concentration. Some of the DBSA could not be accounted for.

Added p-t-butyl thiophenol reacts rapidly at 80 degC and is 90% gone in two weeks. Most of this is probably oxidized to the disulfide.(3) Thus, PBTP and its products cannot be tracked by acid titration. However, a small amount of strong acid is found in the stressed fuel and in the insolubles. Two % of the thiol is found as strong acid in the stressed fuel and one % is found in the insolubles. Thus about 3 % of the thiol is oxidized all the way to a sulfonic acid.

The results on the material balance for chloroacetic acid were mixed. In one fuel the titer on the stressed, filtered fuel was similar to that for the unstressed material. In another fuel, 75 to 95 % of the titratable CA was lost from the liquid fuel after stress. Less than one % of this loss could be accounted for as titratable CA in the insolubles. Bound

(non-titratable) chloride could account for less than one % of the loss (1.2 % Cl in the insolubles x 8 mg/100 mL total insolubles for a fuel blend doped with 6.0 mmol/L of CA).

The overall thrust of the data on DBSA demonstrates that it is an active participant in insolubles formation for the SR/LCO distillate fuel blend. The fact that DBSA is present in the insolubles as titratable strong acid and the fact that the reaction occurs fairly quickly (2 to 5 days at 80 degC to attain a plateau for total insolubles (4)) indicates that the sulfonic acid is involved in salt formation. Corroborating evidence for this viewpoint comes from XPS, which found significant concentrations of sulfur in the oxidized form in the sediment from a DBSA doped fuel blend. The FIMS mol. wt. profile exhibited a large peak at 326, the mass of DBSA, another finding that supports the presence of DBSA in the solid formed during stress.

The earlier theory that acids act as catalysts for forming deposits in SR/LCO blends on the basis of their hydrogen ion concentration (2) must be modified, at least for DBSA. It would appear that DBSA operates in a dual role: (a) acid catalyst for deposit forming reactions and (b) direct participation in insolubles formation by salt formation.

PBTP participates in deposit formation by first oxidizing to p-t-butylbenzene sulfonic acid. This acid can then behave like DBSA, acting in the dual role of acid catalyst and active participant in forming insoluble salts. Only a small fraction of the PBTP converts to acid but the high reactivity of the acid makes it effective at low concentrations. The XPS and FIMS data support the incorporation of the acid in the deposits but direct addition of the thiol to olefins cannot be excluded.

The role of chloroacetic acid in deposit formation cannot be clearly defined on the basis of current knowledge. A theory from earlier work (2), which suggested that CA was acting as an acidic catalyst for deposit formation, may have to be modified.

REFERENCES

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- (2) R. N. Hazlett, Fuel Science & Tech. Int'l., 6, 185 (1988).
- (3) G.W. Mushrush, J.W. Watkins, R.N. Hazlett, D.R. Hardy and H.G. Eaton, Am. Chem. Soc., Fuel Chem. Div. Preprints, 32, 522 (1987).
- (4) R. N. Hazlett and W. Stalick, unpublished data.

TABLE I
Elemental Analysis of Fuel Deposits

Dopant and Conc.	Percent Element							Total
	C	H	N	S	O	Cl	Ash	
None*	77.75	6.08	2.59	1.93	9.38	--	2.24	99.97
DBSA 0.001 M	76.99	6.44	2.53	3.84	9.26	--	0.98	100.04
PBTP 0.03 M	76.86	6.48	1.61	4.42	10.03	--	0.41	99.81
CA 0.01 M	--	--	--	--	--	1.22	--	--

*Deposit formed at ambient temperature. Other deposits formed at 80 degC, two weeks stress.

TABLE II
Percent Atomic Composition of Insolubles by XPS*

Dopant and Conc.	C	O	N	S	Cl
None	79.5	16.5	2.6	1.4	--
DBSA 0.001 M	75.5	18.7	2.9	2.8	--
PBTP 0.03 M	80.5	15.2	1.7	2.5	--
CA	77.0	18.9	2.1	1.3	0.3

*Insolubles formed in 80 degC stress for two weeks
Gulf Coast blend: 20% LCO in SR

TABLE III
Percent Atomic Concentrations of Two Different
Types of Sulfur by XPS

<u>Dopant and Conc.</u>	<u>Reduced Sulfur</u>	<u>Oxidized Sulfur</u>	<u>Total Sulfur</u>
None	0.5	0.9	1.4
DBSA 0.001 M	0.9	1.8	2.8
PBTP 0.03 M	0.6	1.9	2.5
CA 0.01 M	0.6	0.7	1.3

TABLE IV
DBSA Material Balance

<u>Stress</u>	<u>DBSA in Fuel</u>				<u>DBSA Deficit</u>
	<u>DBSA Added</u>	<u>Before Stress</u>	<u>After Stress</u>	<u>DBSA in Insolubles</u>	
80 degC 7 days	-0-	0.00	0.08	0.003	--
80 degC 7 days	1.00	0.96	0.71	0.12	0.13
80 degC 7 days	0.30	0.32	0.17	0.02	0.12
80 degC 14 days	1.00	0.84	0.68	0.15	0.01

DBSA Concentration in mmol/L

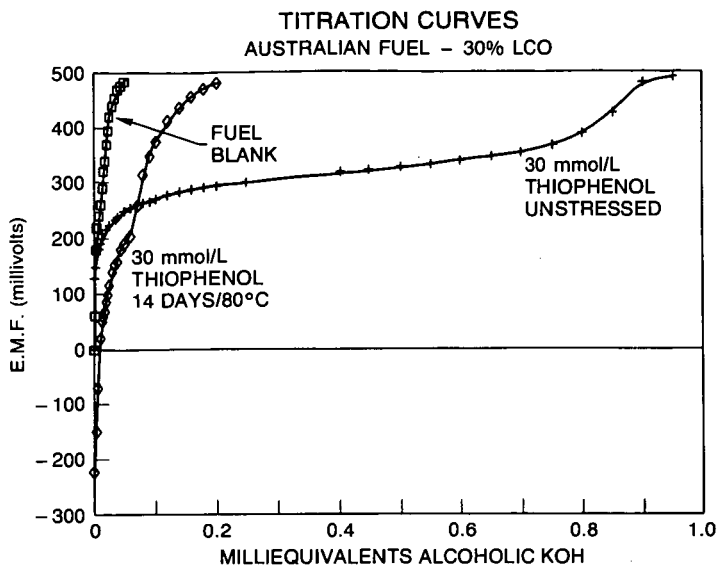


FIGURE 1.

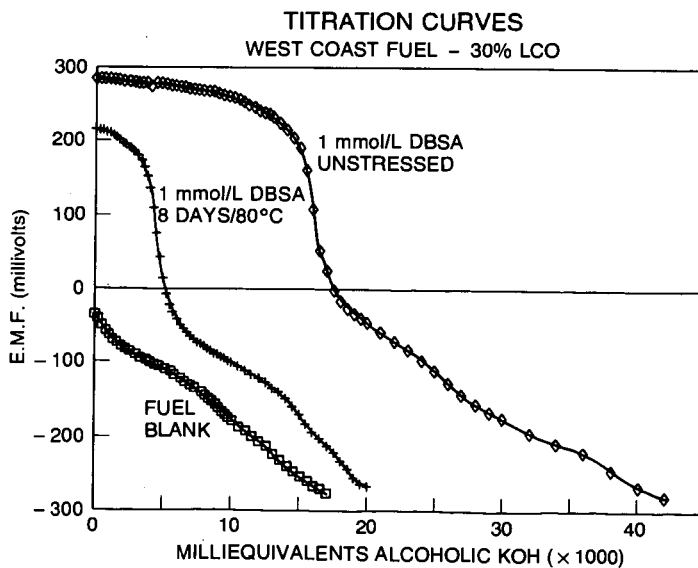


FIGURE 2.